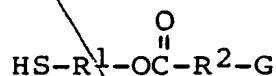


WHAT IS CLAIMED IS:

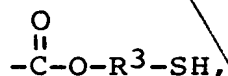
1. In a method for stabilizing a vinyl halide polymer against heat, which comprises incorporating a metal-containing stabilizer therein, the improvement which comprises replacing part of the metal-containing stabilizer with an optionally substituted mercaptohydrocarbylene carboxylate.

2. A method according to Claim 1 in which the mercaptohydrocarbylene carboxylate comprises the reaction product of an optionally substituted mercaptohydrocarbylene-ol with a carboxylic acid.

3. A method according to Claim 1 in which the mercaptohydrocarbylene carboxylate has the formula



where R^1 and R^2 , each independently, is optionally substituted hydrocarbylene and G is hydrogen, carboxy or



where R^3 is optionally substituted hydrocarbylene.

4. A method according to Claim 3 in which R^1 and R^3 , each independently, is alkylene of 2 to 20 carbon atoms, R^2 is alkylene of 1 to 20 carbon atoms and R^1 , R^2 and R^3 each independently is alkenylene of 2 to 20 carbon atoms, cycloalkylene of 3 to 8 carbon atoms, arylene of 6 to 20 carbon atoms, alkarylene of 7 to 40 carbon atoms or aralkylene of 7 to 40 carbon atoms; R^1 , R^2 and R^3 being unsubstituted or substituted by one or more of hydroxy, alkoxy of 1 to 20 carbon atoms, oxo, oxirane, alkoxy-carbonyl of 2 to 20 carbon atoms, aryloxy-carbonyl of 7 to 20 carbon atoms, acyl of 2 to 20 carbon atoms, acyloxy of 2 to 20 carbon atoms, chloro, bromo, iodo, fluoro, cyano, alkylamido of 2 to 20 carbon atoms, mercapto, alkylthio of 1 to 20 carbon atoms, alkyl-sulfamyl of 1 to 20 carbon atoms, alkylsulfonyl

of 1 to 20 carbon atoms, alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms and cycloalkyl of 3 to 8 carbon atoms, and where R^1 , R^2 and R^3 and their substituents are optionally substituted in the chain by one or more of oxygen, sulfur and nitrogen.

B 5. A method according to Claim 4 in which G is hydrogen.

6. A method according to Claim 5 in which R^2 is substituted or unsubstituted alkyl of 1 to 20 carbon atoms or alkenyl of 2 to 20 carbon atoms.

7. A method according to Claim 6 in which R^2 contains 12 to 20 carbon atoms and R^1 is substituted or unsubstituted alkylene of 2 to 20 carbon atoms.

8. A method according to Claim 7 in which R^1 is lower alkylene or hydroxyloweralkylene and R^2 is stearyl, oleyl, linoleyl, myristyl or palmityl.

B 9. A method according to Claim 8 in which the mercapto ester comprises 2-mercaptoethyl stearate, 2-mercaptoethyl oleate, or 2-mercaptoethyl linoleate.

10. A method according to Claim 1 in which the mercaptohydrocarbylene carboxylate comprises an ester obtained by reacting a substituted or unsubstituted mercaptoloweralkanol with a carboxylic acid of 8 to 20 carbon atoms.

3 11. A method according to Claim 4 in which G is

$$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{R}^3-\text{SH} \end{array}$$

12. A method according to Claim 11 in which R^2 is a covalent bond or is substituted or unsubstituted alkylene of 1 to 20 carbon atoms, alkenylene of 2 to 20 carbon atoms, arylene of 6 to 20 carbon atoms, cycloalkylene or cycloalkenylene of 3 to 20 carbon atoms.

13. A method according to Claim 12 in which R¹ and R³, each independently, is unsubstituted or substituted alkylene of 2 to 20 carbon atoms.

14. A method according to Claim 13 in which R² is alkylene of 1 to 20 carbon atoms or alkenylene of 2 to 20 carbon atoms.

15. A method according to Claim 14 in which R¹ and R³ is each lower alkylene or hydroxylower-alkylene.

16. A method according to Claim 4 in which the metal is calcium, barium, zinc, lead, tin or tri-valent antimony.

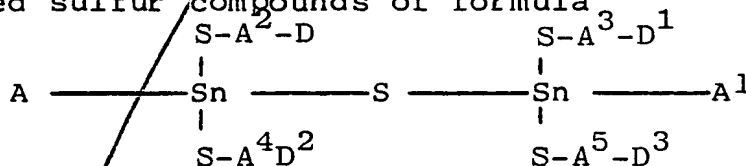
17. A method according to Claim 16 in which the metal is tin.

18. A method according to Claim 17 in which the tin-containing stabilizer comprises a mono- or diorganotin oxide, sulfide, carboxylate, mercaptide, derivative of a mercaptoacid, derivative of a mercaptoalcohol or their esters.

19. A method according to Claim 17 in which the tin-containing stabilizer comprises a compound selected from

dibutyltin maleate
 dibutyltin di(stearyl maleate)
 [monobutyltin(isooctylmercaptoacetate)-sulfide]
 monobutyltin(dodecylmercaptide)sulfide
 monobutyltin(mercaptoethyl oleate)sulfide
 monobutyltin trimercaptoethyl oleate
 monobutyltin(hydroxyethylmercaptide)(sulfide)

and bridged sulfur compounds of formula



where

A and A¹ are lower alkyl of 1 to 12 carbon atoms;

A², A³, A⁴ and A⁵ are lower alkylene

D, D¹, D² and D³ each independently, is

$$\text{OH} - \overset{\text{O}}{\parallel} \text{C} - (\text{C}_8 - \text{C}_{20} \text{ alkyl}),$$

$$-(\text{C}_6 - \text{C}_{18}) \text{ alkyl}, \text{ or where}$$

$$\text{D and D}^1, \text{ or D}^2 \text{ and D}^3 \text{ together form}$$

$$\text{the group}$$

$$-\overset{\text{O}}{\parallel} \text{C} - \text{C}_m \text{H}_{2m} - \overset{\text{O}}{\parallel} \text{C} -$$

where m is a number from 0 to 8.

20. A method according to Claim 1 in which the metal-containing stabilizer is present in an amount to provide up to about 0.25 parts of metal per 100 parts of polymer and the mercapto ester is present in an amount up to about 0.5 parts per 100 parts of polymer.

21. In a method for stabilizing a vinyl halide polymer against heat ^{and light} which comprises incorporating a tin-containing stabilizer therein, the improvement which comprises replacing part of the tin-containing stabilizer with a substituted or unsubstituted mercaptoloweralkanol ester of a carboxylic acid containing from 8 to 20 carbon atoms.

22. A vinyl halide composition which has been stabilized with respect to heat ^{and light} by incorporating therein

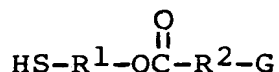
- a) a metal-containing heat stabilizer in which any oxygen present is bonded to one or more of said metal, carbon, phosphorous and hydrogen, said metal-containing stabilizer being introduced in an amount sufficient to provide up to about 0.25 parts of metal per 100 parts of polymer, and

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04/09/81

Sub B3
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JCM
04/08/81

- b) a mercapto ester comprising the reaction product of an optionally substituted mercaptohydrocarbylene-ol with a carboxylic acid, the mercapto ester being introduced in an amount up to about 6.5 parts per 100 parts of polymer.

23. A composition according to Claim 22 in which the metal of the metal-containing heat stabilizer is calcium, barium, zinc, lead, tin or trivalent antimony and the mercapto ester has the formula



where R^1 and R^2 , each independently, is optionally substituted hydrocarbylene and G is hydrogen, carboxy

or $-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{R}^3-\text{SH}$, where R^3 is optionally substituted hydrocarbylene.

24. A composition according to Claim 23 in which R^1 and R^3 , each independently is alkylene of 2 to 20 carbon atoms and R^2 is alkylene of 1 to 20 carbon atoms and R^1 , R^2 and R^3 each independently is alkenylene of 2 to 20 carbon atoms, cycloalkylene of 3 to 8 carbon atoms, arylene of 6 to 20 carbon atoms, alkarylene of 7 to 40 carbon atoms or aralkylene of 7 to 40 carbon atoms; R^1 , R^2 and R^3 being unsubstituted or substituted by one or more of hydroxyl, alkoxy of 1 to 20 carbon atoms, oxo, oxirane, alkoxy-carbonyl of 2 to 20 carbon atoms, aryloxy-carbonyl of 7 to 20 carbon atoms, acyl of 2 to 20 carbon atoms, acyloxy of 2 to 20 carbon atoms, chloro, bromo, iodo, fluoro, cyano, alkylamido of 2 to 20 carbon atoms, mercapto, alkythio of 1 to 20 carbon atoms, alkyl-sulfamyl of 1 to 20 carbon atoms, alkylsulfonyl of 1 to 20 carbon atoms, alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms,

and cycloalkyl of 3 to 8 carbon atoms, and where R¹, R² and R³ and their substituents are optionally substituted in the chain by one or more of oxygen, sulfur and nitrogen.

25. A composition according to Claim ²²24 in which G is hydrogen.

26. A composition according to Claim 25 in which R² is substituted or unsubstituted alkyl of 1 to 20 carbon atoms or alkenyl of 2 to 20 carbon atoms.

27. A composition according to Claim 26 in which R² contains 12 to 20 carbon atoms and R¹ is alkylene of 2 to 20 carbon atoms.

28. A composition according to Claim 27 in which R¹ is lower alkyl or hydroxyloweralkyl and R² is stearyl, oleyl, linoleyl, myristyl or palmityl.

29. A composition according to Claim 28 in which the mercapto ester comprises 2-mercaptoethyl stearate or 2-mercaptoethyl oleate or 2-mercaptoethyl linoleate.

30. A composition according to Claim 22 in which the mercapto ester comprises an ester obtained by reacting a substituted or unsubstituted mercapto-loweralkanol with a carboxylic acid of 8 to 20 carbon atoms.

31. A composition according to Claim ²²24 in which G is $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{R}^3-\text{SH} \end{array}$.

32. A composition according to Claim 31 in which R² is substituted or unsubstituted alkylene of 1 to 20 carbon atoms, alkenylene of 2 to 20 carbon atoms or arylene of 6 to 20 carbon atoms.

33. A composition according to Claim 32 in which R¹ and R³ each independently is unsubstituted or substituted alkylene of 2 to 20 carbon atoms.

34. A composition according to Claim 33 in which R² is alkylene of 1 to 20 carbon atoms or alkenylene of 2 to 20 carbon atoms. *of 2 to 20 carbon atoms*

35. A composition according to Claim 34 in which R^1 and R^3 is each lower alkylene or hydroxylower-alkylene.

36. A composition according to Claim 24 in which the metal is calcium, barium, zinc, tin or trivalent antimony.

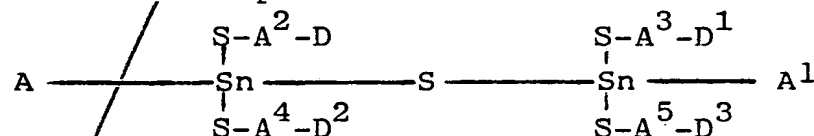
37. A composition according to Claim 36 in which the metal is tin.

38. A composition according to Claim 22 in which the ^{tin}metal-containing stabilizer comprises a mono- or diorgano tin oxide, sulfide, carboxylate, mercaptide, derivative of a mercaptoacid ester or derivative of a mercaptoalcohol or their esters.

39. A composition according to Claim 38 in which the tin-containing stabilizer comprises

dibutyltin maleate
 dibutyltin di(stearyl maleate)
 [monobutyltin(isooctylmercaptoacetate)-sulfide]
 monobutyltin(dodecylmercaptide)sulfide
 monobutyltin(mercaptoethyloleate)sulfide
 monobutyltin trimercaptoethyloleate
 monobutyltin (hydroxyethylmercaptide)(sulfide)

and bridged sulfur compounds of formula



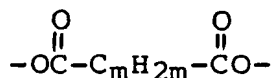
where

A and A^1 are lower alkyl of 1 to 12 carbon atoms;

A^2 , A^3 , A^4 and A^5 are lower alkylene;

D, D¹, D² and D³ each independently,
is

OH, - OC(=O) - (C₈-C₂₀ alkyl),
(C₆-C₁₈)alkyl, or where
D and D¹, or D² and D³ together form
the group



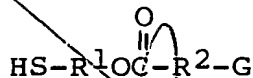
where m is a number from 0 to 8.

40. A composition according to Claim 39 in which
the mercapto ester is a mercaptoloweralkanol ester of a
carboxylic acid of 8 to 20 carbon atoms.

41. A composition comprising

- a) a metal-containing heat stabilizer for
vinyl halide polymers in which any oxygen
atoms present are bonded to one or more
of said metal, carbon, phosphorus and
hydrogen, and
- b) a mercapto ester comprising the reaction
product of an optionally substituted
mercaptohydrocarbylene-ol with a car-
boxylic acid.

42. A composition according to Claim 41 in which
the metal of the metal-containing heat stabilizer is
calcium, barium, zinc, lead, tin or trivalent antimony
and the mercapto ester has the formula



where R¹ and R², each independently, is optionally
substituted hydrocarbylene and G is hydrogen, carboxy
or -C-O-R³-SH, where R³ is optionally substituted
hydrocarbylene.

Sub B4

43. A composition according to Claim 42 in which R^1 and R^3 , each independently, is alkylene of 2 to 20 carbon atoms, R^2 is alkylene of 1 to 20 carbon atoms and R^1 , R^2 and R^3 each independently is alkenylene of 2 to 20 carbon atoms, cycloalkylene of 3 to 8 carbon atoms, arylene of 6 to 20 carbon atoms, alkarylene of 7 to 40 carbon atoms or aralkylene of 7 to 40 carbon atoms; R^1 , R^2 and R^3 being unsubstituted or substituted by one or more of hydroxyl, alkoxy of 1 to 20 carbon atoms, oxo, oxirane, alkoxycarbonyl of 2 to 20 carbon atoms, aryloxy carbonyl of 7 to 20 carbon atoms, acyl of 2 to 20 carbon atoms, acyloxy of 2 to 20 carbon atoms, chloro, bromo, iodo, fluoro, cyano, alkylamido of 2 to 20 carbon atoms, mercapto, alkylthio of 1 to 20 carbon atoms, alkylsulfamyl of 1 to 20 carbon atoms, alkylsulfonyl of 1 to 20 carbon atoms, alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms and cycloalkyl of 3 to 8 carbon atoms, and where R^1 , R^2 and R^3 and their substituents are optionally substituted in the chain by one or more of oxygen, sulfur and nitrogen.

B 44. A composition according to Claim 43 in which G is hydrogen.

45. A composition according to Claim 44 in which R^2 is substituted or unsubstituted alkyl of 1 to 20 carbon atoms or alkenyl of 2 to 20 carbon atoms.

46. A composition according to Claim 45 in which R^2 contains 12 to 20 carbon atoms and R^1 is alkylene of 2 to 20 carbon atoms.

47. A composition according to Claim 46 in which R^1 is lower alkyl or hydroxyl lower alkyl and R^2 is stearyl, oleyl, linoleyl, myristyl or palmityl.

a 48. A composition according to Claim 47 in which the mercapto ester comprises 2-mercaptoethyl stearate/

or 2-mercaptoethyl oleate or 2-mercaptoethyl linoleate.

49. A composition according to Claim 41 in which the mercapto ester comprises an ester obtained by reacting a substituted or unsubstituted mercapto-loweralkanol with a carboxylic acid of 8 to 20 carbon atoms.

50. A composition according to Claim ⁴²~~43~~ in which R^2 is $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{R}^3\text{SH} \end{array}$.

51. A composition according to Claim 50 in which R^2 is substituted or unsubstituted alkylene of 1 to 20 carbon atoms, alkenylene of 2 to 20 carbon atoms or arylene of 6 to 20 carbon atoms.

52. A composition according to Claim 51 in which R^1 and R^3 , each independently, is unsubstituted or substituted alkylene of 2 to 20 carbon atoms.

53. A composition according to Claim 52 in which R^2 is alkylene of 1 to 20 carbon atoms or alkenylene of 2 to 20 carbon atoms.

54. A composition according to Claim 53 in which R^1 and R^3 is lower alkylene or hydroxylower-alkylene.

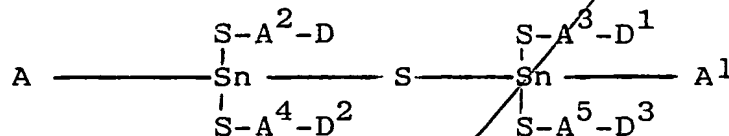
55. A composition according to Claim 43 in which the metal is calcium, barium, zinc, lead, tin or trivalent antimony.

Sub B5 56. A composition according to Claim 43 in which the metal is tin.

57. A composition according to Claim 56 in which the tin-containing stabilizer comprises

dibutyltin maleate
dibutyltin di(stearyl maleate)
[monobutyltin(isooctylmercaptoacetate)-
sulfide]
monobutyltin(dodecylmercaptide)sulfide
monobutyltin(mercaptoethyl oleate)sulfide
monobutyltin(trimercaptoethyl oleate
monobutyltin(hydroxyethylmercaptide)(sul-
fide)

and bridged sulfur compounds of formula

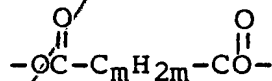


where

A and A¹ are lower alkyl;
A², A³, A⁴ and A⁵ are lower
alkylene;
D, D¹, D² and D³ each independently,

is

OH, - OC(=O) - (C₈-C₂₀ alkyl),
(C₆-C₁₈)alkyl, or where
D and D¹, or D² and D³ together form
the group



where m is a number from 0 to 8.

~~59.~~ A composition according to Claim ~~58~~ in which
the mercapto ester is a substituted or unsubstituted
mercaptoloweralkanol ester of a carboxylic acid of 8 to
20 carbon atoms.

ADD
F6

Add
H¹

Add
5.7

Rule 126
B